Radiochemical Determination of CCRMP Reference Materials for Certification Purposes: Lead 210 Activity Measurements

Final Report

by

Physics Department

The University of Calgary

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources, Canada.

DSS File Number: 26SQ23440-3-9148-7

DSS Contract Serial Number: OSQ83-00169

Canmet Project Number: 380101

Canmet Scientific Authority: Dr. C.W. Smith

Analyst: Dr. C.J. Bland

February 1984

MAY 10 1984

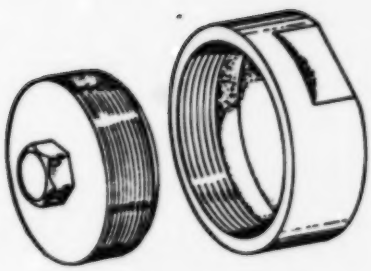
MICROMEDIA

Introduction

Four bottles of CCRM ore samples designated DL-1a, DH-1a, BL-4a and BL-5 were received from CANMET on December 1st 1983. We were requested to determine the activity concentration of ^{210}Pb with reference to a diluted standard (Radiochemical Centre, Amersham) supplied by CANMET. Previous measurements on the ^{226}Ra content of these ores (Smith and Steger 1983) indicated that if secular equilibrium exists in these ores then the ^{210}Pb activity concentrations would vary over about three orders of magnitude ($\sim 1 - 10^3$ Bq/g). To avoid the difficulties associated with the fusion of the samples and the extraction of lead as well as the beta spectrometry of the short-lived daughter, ^{210}Bi, it was decided to measure ^{210}Pb via its direct gamma ray of 47 KeV which arises in about 4% of the decays.

Experimental Method

Due to the low intensity of the gamma radiation emitted and its low energy, it was necessary to use a relatively thin source (few mm) containing as much of the ore sample as possible. Since at an energy of 47 KeV, serious errors may arise due to variations in sample density, the samples were enclosed in a specially designed container which is shown in fig. 1. The PVC container is machined from solid rod. The base is 2 mm thick to minimize absorption of the gamma rays. A lid was screwed down using a calibrated torque wrench (50 ft.-lbs) to achieve the same degree of compaction in all samples. Different quantities of ore were used according to the amount



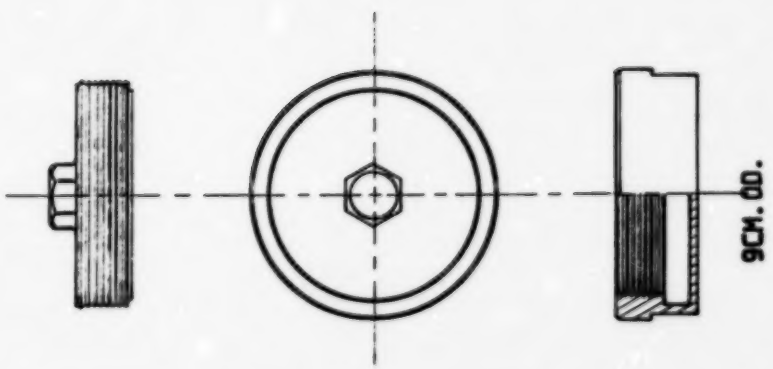


FIGURE 1

CJB

of activity present in each sample, ranging from 30 g for DL-1a to 1g for BL-5. An inert filler (coffee whitener) was added to the smaller samples to achieve the same volume of homogeneous sample for all the ores. The sample assembly was centred in contact with the sensitive area of a hyperpure germanium detector (Princeton Gamma-Tech model IGC-13). The output of the preamplifier (PGT 346) was fed to the input of the main amplifier (Tennelec model 205A) which produced pulses suitable for analysis by a 1024 channel multichannel analyser (Inotech model 5300). The resolution achieved for the ^{210}Pb at 47 KeV was approximately 660 eV (FWHM). The entire energy spectrum from 10 - 130 KeV was sent from the MCA to a desk top mimicomputer (SuperPET) for storage on floppy disc and subsequent data analysis.

In order to compare standards to a standard source of ^{210}Pb emissions, the standard would have to replicate the sample as regards density, chemical composition, grain size etc. Since it is difficult to achieve such similarities, it was decided to determine the ^{210}Pb activity of each sample by the addition to the sample itself of increasing amounts of known activity of ^{210}Pb. The addition must be incorporated in such a way that it is uniformly distributed throughout the sample and causes the minimum change in mass distribution as well as avoiding introducing material with high atomic number. After several tests, the following method was devised.

Standard additions of ^{210}Pb are incorporated into the sample by loading the activity on to small quantities of ion-exchange resin. The ^{210}Pb activity was transferred to the surface of 0.3 g of Bio-Rad

AG1-X4 anion exchange resin from HC1(1.5M)-methanol (83% v/v) solution (Holm, Ballestra and Fukai 1979). This small quantity of resin was mixed into the sample prior to loading in the PVC containers. To ensure replicate counting conditions, 0.3 g of untreated resin was mixed with samples containing no addition of ^{210}Pb standard. Consistent recoveries of >99% ^{210}Pb were measured using the ion exchange procedure.

It should be noted that increasing standard additions were added to different sub-samples, thus any variations between sub-samples are incorporated in the set of 4 measurements made on each ore sample.

Each sub-sample was counted for a sufficient time to achieve counting errors of less than 2%. This generally involved counting times of $\sim 10^5$ secs. The gamma spectrometer was run continuously day and night for 8 weeks in order to obtain all the gamma and background measurements required. Over this period, instrumental drift amounted to less than 1 channel (approximately 200 eV).

Data Analysis

The 47 KeV ^{210} Pb line in ore samples is superimposed on a continuum caused by the Compton scattering of higher energy gamma rays emitted by the sample (e.g. from ^{214}Pb, ^{214}Bi, etc.). This continuum may vary in intensity due to variations in radon emanation in powder samples before and after sealing in the source holder. Several models of multichannel analyser provide a read-out of peak area

and background in a given region of interest. The internal software provided to yield these estimates is generally rather crude and amount to little more than estimating a straight line from the lower to higher energy channels bordering the peak. Since the continuum exhibits a fair amount of curvature, this is not satisfactory for precise peak area estimation. (see Kokta 1973 and references therein). The spectrum of a pure ^{210}Pb source exhibits a Gaussian peak plus a low energy tail caused by incomplete charge collection in the hyperpure germanium detector. A review of various analytical fits to the tail function has been provided by Jorch and Campbell (1977). After examination of the spectrum over an interval form 43 - 50 KeV we concluded that an adequate fit could be achieved by a function of the form:

$$f(x) = a_1 + a_2x + a_3x^2 + a_4 \exp(-(x - a_5)^2/2a_6^2)$$

The last term represents a Gaussian peak whose area is given by:

$$A = \sqrt{2\pi}\, a_4 a_6$$

which is proportional to the strength of the ^{210}Pb source.

In order to determine the best combination of the six constants a_i, in the least squares sense, a programme was written to analyse the spectrum over 46 channels centred on the ^{210}Pb peak. This programme involves inversion of the incremented curvature matrix in order to provide more accurate estimates the constants a_i in order to minimize Chi squared (Marquardt 1963, Bevington 1969). In most cases we were able to obtain adequate fits to the data, so that the reduced Chi squared value was $\lesssim 3$ for 45 degrees of freedom. After transfer from the MCA to the SuperPET, the fitting programme (Gamma

```
DATA ANALYSIS IS
 46 DATA POINTS
AMPLITUDE      = 2231
CHANNEL NO.    = 35.
WIDTH          = 1.
CONSTANT BKGR. = 6006
LINEAR BKGR.   =-15
QUAD. BKGR.    = 0.

WEIGHTING MODE=-1

FIRST CHI SQ= 330513.1137
AMPLITUDE      = 1860.21134 +- 44.7420115
CHANNEL NO.    = 351.611136 +- .0421830573
WIDTH          = 1.777777742 +- .0401361121
CONSTANT BKGR. = 5811.13544 +- 113.648422
LINEAR BKGR.   =-25.34713814 +- .7668838861
QUAD. BKGR.    = .0007302813 +- 1.150825164E-05

NEW CHI SQ = 754.8116811

FIRST CHI SQ= 754.8116808
AMPLITUDE      = 1806.61547 +- 43.8376611
CHANNEL NO.    = 351.577148 +- .0424606827
WIDTH          = 1.717713398 +- .0434677821
CONSTANT BKGR. = 5715.93364 +- 328.876647
LINEAR BKGR.   =-25.6440471 +- 2.41384175
QUAD. BKGR.    = .0020828859 +- 4.967113178-05

NEW CHI SQ = 22.11622E+

FIRST CHI SQ= 22.11622E4
AMPLITUDE      = 1805.18263 +- 43.7874127
CHANNEL NO.    = 351.573483 +- .0429873627
WIDTH          = 1.731188111 +- .0431657554
CONSTANT BKGR. = 5496.43535 +- 913.183E13
LINEAR BKGR.   =-23.7772417 +- 7.0735941
QUAD. BKGR.    = .0456153362 +- .0149136087

NEW CHI SQ = 3.79526227

FIRST CHI SQ= 3.79516227
AMPLITUDE      = 1802.62824 +- 43.9332725
CHANNEL NO.    = 350.575555 +- .0430861291
WIDTH          = 1.7361114? +- .0442617962
CONSTANT BKGR. = 4226.45742 +- 2219.91378
LINEAR BKGR.   =-17.575545 +- 17.9661686
QUAD. BKGR.    = .0244391513 +- .0062546065

NEW CHI SQ = 3.31477433
```

FIGURE 2

Regina) was run using 46 data points. Four to five iterations were normally required to achieve an optimum fit after entering the initial estimate for the six constants a_i. An example of the print-out during a typical run is shown in fig. 2. After fitting, the data points and the the fitted function are plotted on a chart recorder. Fig. 3 shows a typical plot obtained during this project.

The uncertainty in each parameter in the least squares fit is related to the diagonal terms in the error matrix. In most of the 16 samples measured the error in the amplitude and width of the fitted Gaussian are approximately 1 - 2% each. According to the Bevington the true area of the peak is related to the calculated area ($\sqrt{2\pi}\, A\sigma$) by the equation:

$$(\text{True Area}) = (\text{Calculated Area}) + \chi^2$$

We have treated the calculated true area as integral counts N, to which we should ascribe a Poissonian deviation of $\sqrt{N}$.

If various quantities X are added to the sample, the count rate Y should be given by:

$$Y = K(X + A) + B$$

where K is a constant, A is the intrinsic activity of the sample and B is the background count rate for the ^{210}Pb line. If Y is plotted against X the intrinsic activity is given by

$$A = \frac{\text{Intercept - Background}}{\text{Slope}}$$

In order to estimate the slope and the intercept, we wish to fit a straight line to data consisting of counts C_i (derived from the area

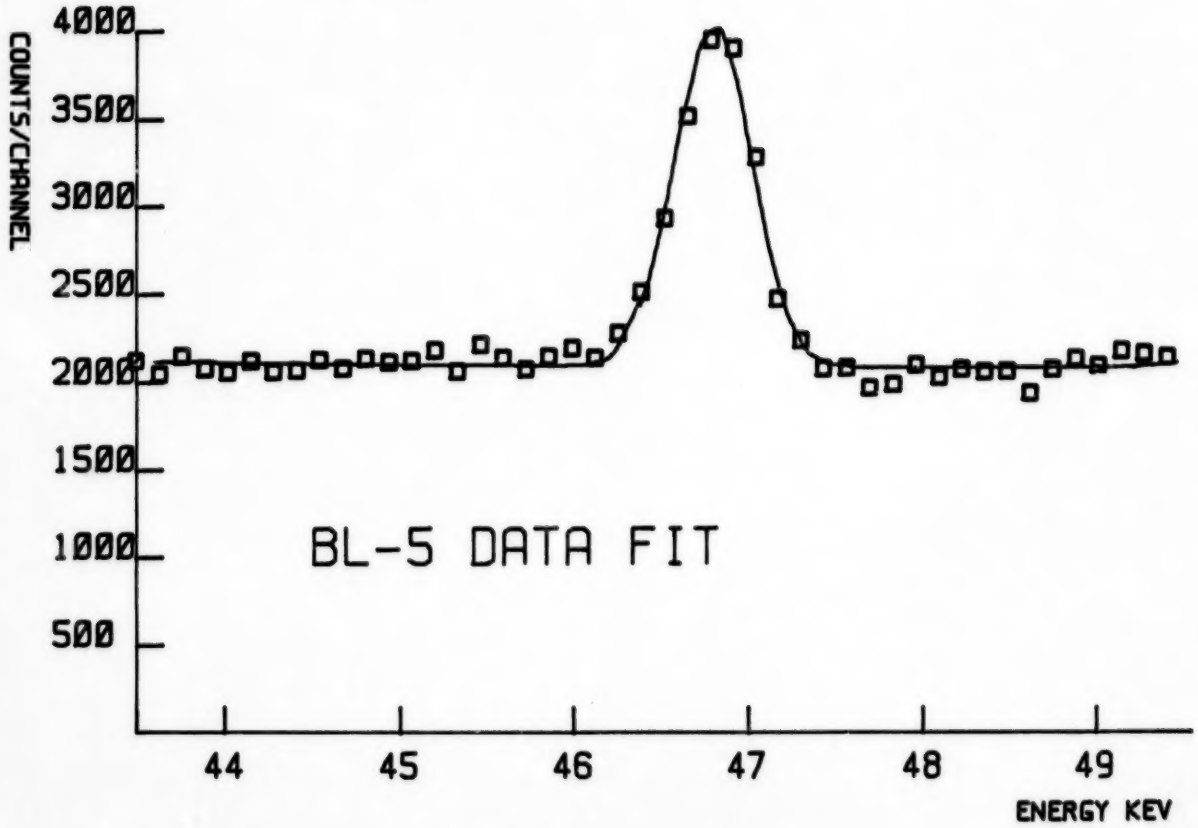

COUNTS/CHANNEL
4000
3500
3000
2500
2000
1500
1000
500
BL-5 DATA FIT
44
45
46
47
48
49
ENERGY KEV

FIGURE 3

of the Gaussian) made over intervals of time t_i for each of a number of values n_i (in this case incremental additions of standard activity). The statistical model to be fitted is:

$$y_i = f(x_i) + z_i$$

where z_i is a random error with zero mean and variance $f(x_i)/t_i$ (Cooper 1969). We begin by computing the least squares fit straight line by using the observed value y_i in the weights:

$$W_{1i} = t_i/y_i$$

The fitting process using these weights estimates the slope and intercept of the function $f(x_i)$ and new weights for the next iteration may be calculated from:

$$W_{2i} = t_i/f(x_i)$$

The process continues until the estimated parameters remain essentially constant from one iteration to the next. At the end of this process the fit is described by a line

$$y = bx + a$$

with slope b and intercept a. The activity within the sample is thus given by

$$A = \frac{a - B}{b} \text{ Bq.} \quad \text{(where b is in cps. Bq}^{-1}\text{)}$$

where B is the groundground count rate. The specific activity is $\frac{A}{M}$ where M is the mass of the sample.

Error Analysis

The variance of the derived total activity:

$$A = \frac{a - B}{b}$$

may be derived from the standard error propogation formula:

$$\sigma_A^2 = \sigma_a^2 \left(\frac{\partial A}{\partial a}\right)^2 + \sigma_b^2 \left(\frac{\partial A}{\partial b}\right)^2 + \sigma_B^2 \left(\frac{\partial A}{\partial B}\right)^2$$

whence

$$\sigma_A^2 = \frac{1}{b^2} (\sigma_a^2 + \sigma_B^2 + A^2\sigma_b^2)$$

It may be that the variance of the intercept of the weighted least squares fit is given by:

$$\sigma_a^2 \triangleq \frac{1}{\Delta} \sum \omega_i x_i^2$$

where ω_i are the wights used in the final iteration and:

$$\Delta = \sum \omega_i \sum \omega_i x_i^2 - \left(\sum \omega_i x_i\right)^2$$

The variance of the slope is given by

$$\sigma_b^2 \triangleq \frac{1}{\Delta} \sum \omega_i$$

The variance of the background is simply

$$\sigma_B = \frac{\sqrt{N_B}}{t_B}$$

where N_B is the counts in the background peak and t_B the time during which they were accumulated.

Having obtained the variance of the total activity, the variance of the specific activity is given by:

$$\sigma_s^2 = \frac{1}{M^2}\left(\sigma_A^2 + \left(\frac{A}{M}\right)^2 \sigma_M^2\right)$$

where M is the mass of the sample and σ_M is the estimated variance of the mass determination.

No attempt has been made to include the uncertainties in the activities of the standard additions of ^{210}Pb reference solutions. The CCRMP lead 210 reference solutions supplied by CANMET were used for most of the measurements. This solution was prepared by diluting Amersham RBZ-44 solution SO/8/54 (certificate P18537). Since the measurement method used required rather large amounts of reference solution, more Amersham soiution was purchased and diluted by exactly the procedure described for the CCRMP solution. This additional reference material is obtained from Amersham RBZ-44, solution SO/8/63 (certificate number P19879). As far as can be determined this is identical to the solution used by CANMET, except that the reference time is quoted as 1 May 1981 i.e. one year later than the original solution. This one year difference has been taken into account in calculating the activity added to a few of the samples, using a half life of 22.3 years. The activity of the standard addition made to each subsample was calculated according to the day on which the measurement was made. For the sample DL-1a, additions of 2, 4 and 6 mℓ were made. In the remaining samples, additions of 5, 10 and 15 mℓ were made. Due to an error in the case of BL5, a duplicate addition of 10 mℓ was made instead of 15 mℓ. Fortunately the second 10 mℓ used had a slightly higher activity than the first since it was prepared from the newer Amersham standard.

No attempt has been made to make any corrections for uncertainties

in the standard activities added. Any errors in the volumes added are likely to be proportionally much smaller then the uncertainty quoted for the ^{210}Pb activity by Amersham.

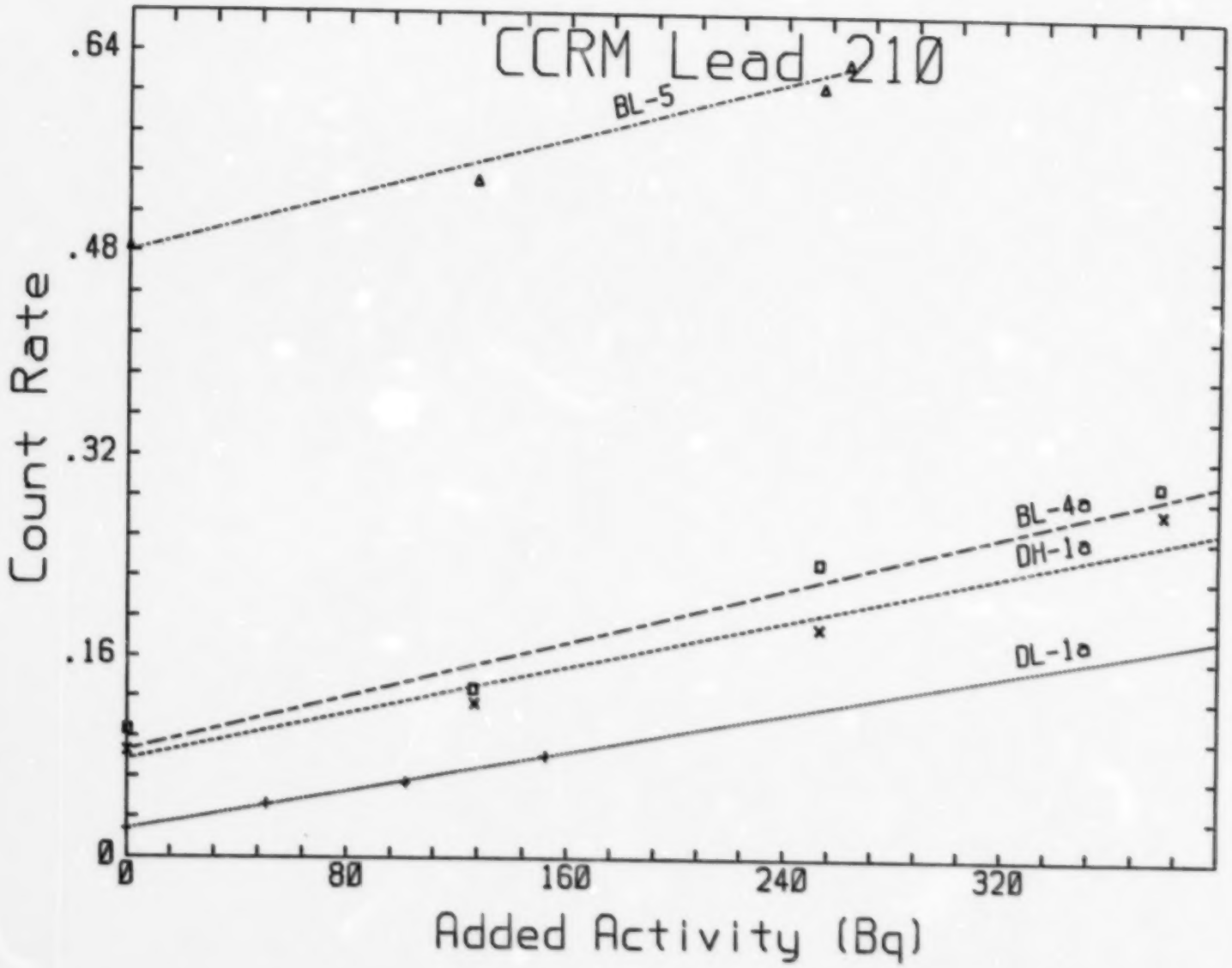
Results

Tables 1 to 4 summarizes the counting data for the 16 sub-samples measured. The Gaussian widths and amplitudes are used to derive the peak area which is then corrected by the Chi squared correction to yield the total number of counts. This is then divided by the live time value to obtain the count rate.

Using a programme written for the SuperPET, the x_i values (added activity), y_i values (corrected area i.e. counts) and t_i values (live times) were used to compute the best fit straight line. The programme (Poisson Supreme) uses the weighting procedure described previously and iterates until successive slopes and intercepts remain essentially constant. The specific activity and its variance are then calculated according to the procedure described above.

Fig. 4 is a composite graph showing all the data as well as the four linear fits obtained for the four ore samples. The symbols used to plot the data points (crosses, squares, etc.) are not dimensioned to illustrate the error ranges. It may be noted that the correlation with a linear fit is quite good (the conventional correlation coefficient is not meaningful since the y data is not drawn from a normal population). Some data points deviate from the regression lines by more than would be expected from the variance calculated from the

FIGURE 4


CCRM Lead 210
BL-5
BL-4σ
DH-1σ
DL-1σ
Count Rate
.64
.48
.32
.16
0
0
80
160
240
320
Added Activity (Bq)

square root of the counts. A more rigorous statistical treatment would require that the variance of the independent variable (added activity) be taken into account. This variance derives from the error caused by incomplete transfer of the small amount of ion exchange resin from the column to the sample as well as possible incomplete mixing of the resin with the sample. We should also stress that these data were derived from four separate sub-samples of each sample, therefore the data points also may reflect any deviations from homogenuity in the ^{210}Pb activity within the samples supplied, as well as the errors associated with separate weighings and the addition of the ion exchange resin carrying the standard added activity.

Acknowledgements

P. Overend did most of the sample preparation and ion exchange procedures. J.G. Dufour provided valuable assistance in data transfer and the running of the data fitting programme. The use of Physics department facilities wasmade available by kind permission of Dr. T. Mathews.

References

Bevington, P.R., "Data Reduction and Error Analysis for the Physical Sciences", McGraw Hill, 1969.

Cooper, B.E., "Statistics for Experimentalists", Pergamon Press, 1969.

Holm, E. Ballestra, S and Fukai, R., Talanta, 26, 791-794, 1979.

Jorch, H.H. and Campbell, J.L., Nucl. Inst. and Methods, 143, 551-559, 1977.

Kokta, L., Nucl. Inst. and Methods, 112, 245-251, 1973.

Marquardt, D., J. Soc. Ind. Appl. Math. 11, 2, 431-441, 1963.

Smith, C.W. and Steger, H.F., CANMET report 83-9E, Energy, Mines and Resources Canada, May 1983.

Table 1

CCRM Lead 210 Determination

Sample DL-1a

Weight 30.0 ± 0.2 g

Date	Activity Added (Bq.)	Live Counting Time(sec)	L.S.F Gaussian Amp.	L.S.F Gaussian Width	Area Peak	Chi Squared Corr.	Corrected Area	Count Rate (/sec)	Remarks
27/12/83	0	332100	1816.1	1.585	7215.4	59.4	7274.8	2.19×10^{-2}	
11/12/83	50.55	239900	1938.0	2.079	10103.1	90.5	10193.6	4.25×10^{-2}	
13/12/83	101.1	99510	1042.3	2.209	5770.1	188.6	5958.7	5.99×10^{-2}	
14/12/83	151.6	82100	1619.1	1.612	6541.9	150.3	6692.2	8.15×10^{-2}	

Background Count Rate(/sec)= 4.34×10^{-3}

Slope (Iterative weighted L.S.F.)= 3.902×10^{-4}

Intercept= 0.02203

Derived Specific Activity (Bq/g)= 1.568 ± .037

Table 2

CCRM Lead 210 Determination

Sample DH-1a

Weight 5.00 ± 0.05 g

Date	Activity Added (Bq.)	Live Counting Time(sec)	L.S.F Gaussian Amp.	L.S.F Gaussian Width	Area Peak	Chi Squared Corr.	Corrected Area	Count Rate (/sec)	Remarks
20/12/83	0	86300	1691.3	1.691	7168.9	106.7	7275.6	8.43×10^{-2}	
21/12/83	126.3	84285	2359.6	1.727	10215	150.8	10365.8	12.30×10^{-2}	
22/12/83	252.5	85675	3164.0	1.972	15640	142.7	15782.7	$18.42.10^{-2}$	
23/12/83	378.8	63900	4030.6	1.733	17509	271.8	17780.8	27.82×10^{-2}	

Background Count Rate(/sec)= 4.34×10^{-3}

Slope (Iterative weighted L.S.F.)= 4.656×10^{-4}

Intercept= 0.0778

Derived Specific Activity (Bq/g)= 31.83 ± 0.60

Table 3

CCRM Lead 210 Determination

Sample BL-4a

Weight 10.0 ± 0.1 g

Date	Activity Added (Bq.)	Live Counting Time(sec)	L.S.F Gaussian Amp.	L.S.F Gaussian Width	Area Peak	Chi Squared Corr.	Corrected Area	Count Rate (/sec)	Remarks
26/01/84	0	85500	1902.6	1.786	8517.6	149.4	8667.0	1.014×10^{-1}	
23/01/84	125.9	249300	7583.2	1.745	33165.6	435.6	33601.2	1.348×10^{-1}	
02/01/84	252.3	157700	8578.6	1.702	36600.9	595.6	37196.5	2.359×10^{-1}	
25/01/84	377.7	88250	6135.8	1.693	26043.2	470.3	26513.5	3.004×10^{-1}	

Background Count Rate(/sec)= 4.34×10^{-3}

Slope (Iterative weighted L.S.F.)= 5.424×10^{-4}

Intercept= 0.0849

Derived Specific Activity (Bq/g)= 14.97 ± 0.25

Table 4

CCRM Lead 210 Determination

Sample BL-5

Weight 1.00 ± 0.02 g

Date	Activity Added (Bq.)	Live Counting Time(sec)	L.S.F Gaussian Amp.	L.S.F Gaussian Width	Area Peak	Chi Squared Corr.	Corrected Area	Count Rate (/sec)	Remarks
22/12/83	0	19000	2103.6	1.725	9095.8	104.0	9199.8	4.84×10^{-1}	
23/12/83	126.3	13200	1619.2	1.726	7005.4	98.1	7103.5	5.38×10^{-1}	
28/12/83	252.4	20100	2818.2	1.722	12164.5	196.7	12361.2	6.15×10^{-1}	
06/01/84	261.5	79100	11369	1.733	49387.7	729	50116.7	6.34×10^{-1}	10mℓ new spike added rather than 15mℓ

Background Count Rate(/sec)= 4.34×10^{-3}

Slope (iterative weighted L.S.F.)= 5.750×10^{-4}

Intercept= 0.480

Derived Specific Activity (Bq/g)= 827.7 ± 35.4